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A comparative study of straw, perennial grasses and hardwoods in terms of fast pyrolysis products

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HIGHLIGHTS

- ▶ Thermochemical properties of biomass in terms of fast pyrolysis products were compared.
- ▶ Crops selected for this study were: straw, perennial grasses and hardwoods.
- ▶ Bio-oil from switch grass has the highest potential for the production of chemicals.
- ▶ Switch grass gives the highest yields of levoglucosan and furfural.
- ▶ Willow SRC is also an attractive energy feedstock for fast pyrolysis processing.

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ABSTRACT

The aim of this study is to characterise and compare fast pyrolysis product yields from straw, high yielding perennial grasses and hardwoods. Feedstocks selected for this study include: wheat straw (*Triticum aestivum*), switch grass (*Panicum virgatum*), miscanthus (*Miscanthus x giganteus*), willow short rotation coppice (*Salix viminalis*) and beech wood (*Fagus sylvatica*). The experimental work is divided into two sections: analytical (TGA and Py-GC–MS) and laboratory scale processing using a continuously fed bubbling fluidized bed reactor with a capacity of up to 1 kg/h. Pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS) has been used to quantify pyrolysis products and simulate fast pyrolysis heating rates, in order to study potential key light and medium volatile decomposition products found in these feedstocks. Py-GC–MS quantification results show that the highest yields of furfural (0.57 wt.%), 2-furanmethanol (0.18 wt.%), levoglucosan (0.73 wt.%), 1,2-benzenediol (0.27 wt.%) and 2-methoxy-4-vinylphenol (0.38 wt.%) were found in switch grass, and that willow SRC produced the highest yield of phenol (0.33 wt.%). The bio-oil higher heating value was highest for switch grass (22.3 MJ/kg). Water content within the bio-oil is highest in the straw and perennial grasses and lowest in the hardwood willow SRC. The high bio-oil and char heating value and low water content found in willow SRC, makes this crop an attractive energy feedstock for fast pyrolysis processing, if the associated production costs and harvest yields can be maintained at current reported values. The bio-oil from switch grass has the highest potential for the production of high value chemicals.

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1. Introduction

Biomass is expected to contribute to over half of the renewable energy demand by 2020 [1]. To achieve this goal, biomass supplies in the UK need to be increased, sustained and further sourced. Dedicated high yielding energy grasses and hardwoods will need to be utilised, alongside other waste forms of biomass, such as straws. These feedstocks can be converted to energy and high value chemicals via a number of processes including thermal, biological, and mechanical or physical processes. Fast pyrolysis, a thermal process, is a possible conversion route that offers promising advantages and is of particular interest. This is because bio-oil, the main pyrolysis product (up to 75 wt.% for wood on dry basis), offers greater versatility in its storage, transport and application and can be used as either a source of energy or chemicals [2]. According to McKendry, biomass can be classified into any of the following four categories or a combination of these: (1) herbaceous plants and grasses, (2) woody plants, (3) aquatic plants and (4) manure [3]. In this study, herbaceous plants and grasses and woody plants are investigated. Cellulose, hemicellulose and lignin are the three main components found in these categories (1 and 2). There is a considerable difference in the chemical structure found in each of these components. The differences should be taken into consideration because this

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will influence pyrolysis product yields and the chemical makeup of bio-oil.

Cellulose consists of a two sugar repeating unit known as cellobiose, and is able to form straight chains due to the β-1,4 linkages. The cellulose chain is hydrophilic along its sides and hydrophobic on its end. Interaction between cellulose chains by intermolecular hydrogen bonding allows chains to adhere to one another and form ordered crystalline material, known as microfibril [4]. Hydrogen bonding occurs between the aliphatic hydrogen atoms and the principle functional groups, the hydroxyl groups [5]. Microfibrils are connected and held together by cross-linking glycan molecules to form fibres. The degree of polymerisation ranges between 1000 and 15,000 [6,7], with an average molecular weight of 100,000 [3]. Most wood derived cellulose is approximately 35% amorphous [6]. The crystalline surfaces and amorphous regions of cellulose are thought to be most accessible to water, chemicals and microorganisms [7]. The centre crystalline region has very limited accessibility because of the tight chain packing.

Hemicellulose is a cross-linking amorphous glycan that binds together cellulose microfibrils, and this contributes to its structural integrity [4]. The degree of polymerisation found in hemicellulose is significantly lower than that of cellulose, ranging from 100 to 200 [6]. The hemicellulose backbone is usually made up of a single monomer that is hydrogen bonded to the cellulose microfibrils [4]. The backbone and the protruding short sugars side chains vary with plant species and age. Hemicellulose is classified according to its compositional units, molar ratios and linkages. Galactoglucommans (5–15 wt.%) and arabinoglucuronoxylan (7–10 wt.%) are common types of hemicellulose found in softwood, and hardwood hemicellulose usually contains both glucuronoxylan (15–30 wt.%) and glucomannan (2–5 wt.%) [7].

Lignin is the main binder for cellulosic components and is considered an encrusting material [6,8]. The precursors of lignin are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [6]. Confieryl alcohol and sinapyl alcohol are both methoxylated. The methoxyl content in hardwood is higher than that of softwoods. This is because the main precursors for hardwoods are coniferyl alcohol and sinapyl alcohol. The main precursors in softwoods are coniferyl alcohol and minor amounts of p-coumaryl alcohol [6], p-coumaryl alcohol is commonly found in grasses [3].

The compositional content, harvest yields and associated production cost of feedstocks investigated here, are reported in Table 1. Cellulose content is seen to be highest for the perennial grass miscanthus and the hardwood willow SRC. In comparison to the other crops, willow SRC has the lowest hemicellulose content. The lignin content is generally reported to be highest for the hardwoods. Wheat is commercially grown for its grain and the straw remaining, approximately half the original crop, is available for bioenergy use. Consequently, the yield per hectare and the associated production cost is significantly lower than that of the other dedicated energy crops. However, wheat straw does have a low-grade commercial market which may interfere with its sole use for bioenergy. Although yields and costs are higher for dedicated energy crops, such as perennial grasses and hardwoods such as willow SRC, the additional land requirement could be potentially problematic in the future. Hardwoods, such as beech wood, are less desired bio-energy feedstocks, because of their long growth period. Beech wood has been used here as a reference material for comparison. This is because the pyrolytic behaviour of beech wood is well-documented [26].

The aim of this study is to characterise these feedstocks and compare fast pyrolysis products and yields from straw, high yielding perennial grasses and hardwoods. This topic has received much interest in the literature and some of the findings from previous studies which are shown in Table 2. The reported product yields vary considerably between studies, and this is thought to be mainly related to differences in the reactor type, experimental set-up, processing capacity and the feedstock source.

The experimental work reported here is divided into two sections: analytical, with and without close-coupled analysis, and laboratory scale processing using a continuously fed bubbling fluidized bed reactor with a capacity of up to 1 kg/h, with decoupled

Table 1
Crop composition, harvest yields and estimated production cost.

Feedstock	Yield and costs		Composition			References	Additional comments
	Harvest yields	Cost to produce	Cellulose	Hemicellulose	Lignin		
	(t/ha/y on dry basis)	[£/t]	[wt.% d.b]				
Wheat straw	3.10[a]	∼20.00[b]	33.20	24.00	15.10	[1,10]	
	–	–	–	–	7.50	[11]	
	–	–	39.90	28.20	16.70	[12]	
	–	–	45.37	28.28	18.74	[13]	
	–	–	41.30	30.80	7.70	[14]	
			38.20	24.70	23.40	[24]	
Switch grass	5.40–9.60	30.00–57.00	36.00	31.60	6.10	[15,10]	
	–	–	–	–	8.56	[16]	
	–	–	44.90	31.40	12.00	[24]	Late cut
Miscanthus	–	–	54.00	23.90	14.94	[17]	Treatment 1
	10.00–15.00	–	–	–	–	[18]	
	–	–	52.13	25.70	12.50	[19]	
	17.69	–	–	–	–	[20]	Mean: 2002
	–	30.24	–	–	–	[21]	Local use (12.5 t/ha/y)
Willow SRC	–	–	49.30	14.10	20.00	[14]	
	∼10.00	–	–	–	–	[22]	
	–	–	–	–	19.00	[16]	
	–	–	–	–	19.60	[11]	
	8.00	31.00	–	–	–	[23]	
Beech wood	–	–	43.30	31.80	24.40	[25]	
	–	–	40.10	26.80	23.20	[12]	

d.b – dry basis.

[a] Straw (on average – wheat straw ∼45% of whole crop [9].

[b] Main cost of production allocated to the production of the grain, hence its low cost (bailing, carting and fertiliser).

Table 2
Fast pyrolysis product yields.

Feedstock	Fast pyrolysis reactor[a]		Product yields					References
	Reactor capacity	Process temperature	Liquid			Char	Gas	
	(kg/h)	(°C)	Bio-oil[b] (wt.% w.f)	Organics (wt.% d.b)	Reaction water (wt.%)	(wt.% d.b)	(wt.% d.b)	
Wheat straw	0.15	509	–	24.90	–	31.90	15.60	[11]
	1.50	505	60.60		–	21.70	17.10	S run 4 [27]
Switch grass	0.15	500	–	51.50	–	24.70	7.90	[11]
	5.00	500	–	~40.00	–	~25.00	-	10% Moisture [45]
	2.50	480	60.70	–	–	12.90	11.30	[28]
	0.10	500	60.20	–	–	18.80	13.60	Run 1 [29]
Miscanthus	0.15	500	–	52.38	8.93	19.17	11.10	Treatment 1: [17]
Willow SRC	1.00	500	–	40.51	10.83	19.28	19.89	[30]
	0.15	507	–	52.90	–	20.90	9.30	[11]
Beech wood	1.50	498	67.80	–	–	12.60	13.30	B run 2 [27]
	1.50	500	65.00	–	–	15.90	17.70	[31]
	1.00	500	62.46[d.b]	–	–	17.02	17.41	[32]

d.b – dry basis; w.f – wet feed.
[a] Continuous bubbling fluidised bed reactor.
[b] Bio-oil includes the organics, reaction water and initial feedstock moisture.

liquid and char analysis. Py-GC–MS has been used to quantify and simulate fast pyrolysis heating rates in order to study potential key light and medium volatile decomposition products found in these feedstocks. Our literature review failed to identify studies that have quantified key light and medium volatile decomposition products found in these feedstocks. Results from this study will contribute to the existing knowledge of crop pyrolysis yields and products, and will provide a better comparison of the different feedstocks and their potential for use and upgrading.

2. Materials and methods

2.1. Materials

Switch grass (*Panicum virgatum*) and miscanthus (*Miscanthus x giganteus*) were grown on sandy soil less attractive for food production, at Woburn experimental farm in Bedfordshire, UK (52 01°N, 00 36°W, ca. 90 m AOD). Fertiliser was only applied in the first year and the crops were harvest annually. Switch grass was harvested in late winter, once the crop had fully senesced, and miscanthus was harvested during spring. Wheat straw (*Triticum aestivum*), a crop commercially produced for its grain, was obtained from Rothamsted experimental farm in Harpenden. Willow SRC (*Salix viminalis*) was oven dried at 80 °C for 36 h and obtained from Coppice Resources Ltd., Redford (UK). Beech wood (*Fagus sylvatica*) was purchased from J. Rettenmaier & Söhne GmbH + Co. Rosenberg (Germany). Once the crops were harvested with the exception for willow SRC and beech wood, they were immediately removed from the field and dried in a re-circulating oven for 36 h at 80 °C. The dried material was then milled, using a cutting mill with a 1 mm sieve, and then stored at room temperature pending further analysis. The particle size fractions used for analytical analyses and fast pyrolysis processing were between 150–250 μm and 250–1000 μm respectively.

2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using the PerkinElmer Pyris 1 analyser. Approximately 3 mg of analytical sample was pyrolysed to 900 °C at a heating rate of 25 °C/min, and held at that temperature for 15 min at a nitrogen purge flow rate of 30 ml/min. The combustion studies followed the same temperature program as above with an air purge flow rate of 30 ml/min.

2.3. Ash content analysis

The ash content of the biomass and fast pyrolysis char samples was derived by ashing approximately 2 g of material at 575 °C for 6 h (ASTM E1755 – 01-2007). The moisture content of all samples prior the ash content analysis was carried out using a Sartorius MA35 moisture analyser, in which a sample of about 1 g was placed in an aluminium pan and then dried at 105 °C to a constant weight. The reported data for ash and moisture content were the average of three measurements.

2.4. Elemental analysis and heating values

A Carlo-Erba EA1108 elemental analyser was used to determine the carbon, hydrogen and nitrogen content (wt.%). Oxygen was determined by difference. The samples were analysed in duplicate and an average value was taken. Inorganic content was determined using the PerkinElmer Optima 7300DV Induced Coupled Plasma (ICP) Emission Spectrometer. The samples were digested prior to analysis and analysed in triplicate; average values are shown.

The higher heating value (HHVdry) was calculated using Eq. (1) [33], and the lower heating value (LHVdry) was calculated using the following [34]

$$\begin{aligned} \mathrm{HHV_{dry}}\ (\mathrm{MJ/kg}) : 0.3491 \cdot \mathrm{C} + 1.1783 \cdot \mathrm{H} + 0.1005 \cdot \mathrm{S} \\ - 0.1034 \cdot \mathrm{O} - 0.0151 \cdot \mathrm{N} - 0.0211 \cdot \mathrm{ash} \end{aligned} \tag{1}$$

$$\mathrm{LHV_{dry}}\ (\mathrm{MJ/kg}) : \mathrm{HHV_{dry}} - 2.442 \times 8.936 \times (\mathrm{H}/100) \tag{2}$$

where C, H, N, O and S wt.% on dry basis

The higher and lower heating values of the bio-oils, on wet basis (as-received), were calculated using the following equations [34]

$$\mathrm{HHV_{a.r}}\ (\mathrm{MJ/kg}) : \mathrm{HHV_{dry}} \times (1 - \mathrm{H_2O}/100) \tag{3}$$

$$\begin{aligned} \mathrm{LHV_{a.r}}\ (\mathrm{MJ/kg}) : \mathrm{LHV_{dry}} \times (1 - \mathrm{H_2O}/100) - 2.442 \\ \times (\mathrm{H_2O}/100) \end{aligned} \tag{4}$$

where H_2O in wt.%.

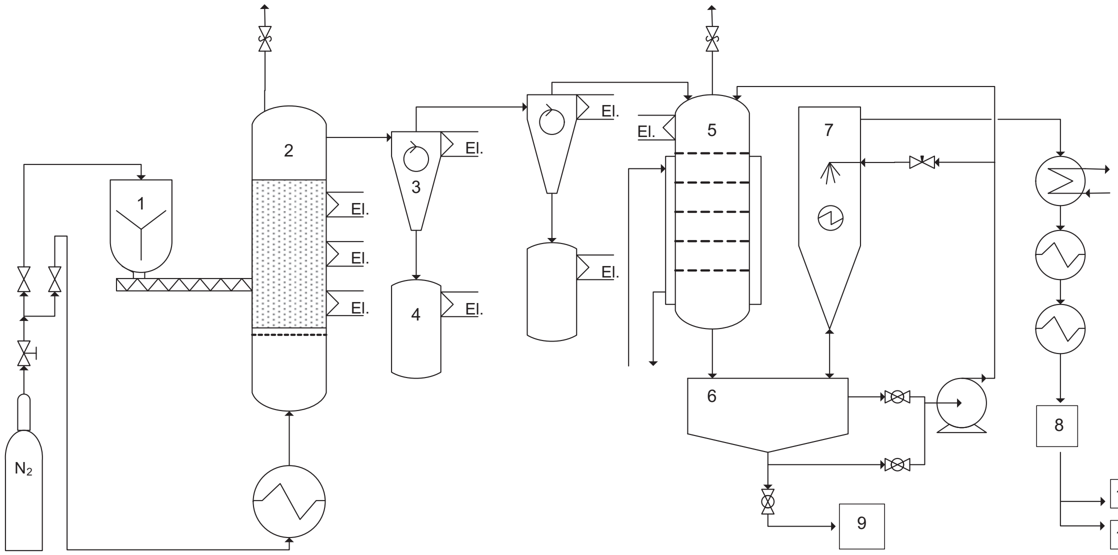

Fig. 1. Fast pyrolysis rig set-up: (1) – feed hopper, (2) – reactor, (3) – cyclone, (4) – char pot, (5) – quench column, (6) – common tank, (7) – electrostatic precipitator, (8) – gas counter, (9) – liquid out, (10) – GC, and (11) – gas out.

2.5. Pyrolysis – gas chromatography–mass spectrometry (Py-GC–MS)

2.5.1. Analytical pyrolysis

For each feedstock, a sample of approximately 3 mg was pyrolysed using a CDS 5200 pyrolyser coupled to a Varian 450-GC chromatograph and 220-MS mass spectrometer, to a pyrolysis temperature of 520 °C (held for 15.0 s at 520 °C) at a heating rate of 20 °C/ms. A Varian factorFour column was used (30 m, 0.25 mm id., 0.25 μm df). The GC oven was held at 45 °C for 2.5 min, then heated at 5 °C/min to 250 °C and held at this temperature for 7.5 min. A heated transfer line, maintained at 310 °C, was used to transfer the devolatilised components onto the GC column via the PTV1070 type injection port held at 275 °C. Proposed Assignments (m/z = 45–300) were made from mass spectra detection using the NIST05 MS library and from assignments in the literature [35,36].

2.5.2. Compound quantification

Compounds purchased from Sigma Aldrich were used for the calibration, and are as follows: 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde); 4-hydroxy-3-methoxybenzaldehyde (vanillin); 2-methoxy-4-methylphenol (creosol); 2-furanmethanol (furfuryl alcohol); furan-2-carbaldehyde (furfural); 2-methoxyphenol (guaiacol); 2-methoxy-4-vinylphenol; phenol; 3-methoxycatechol (p-cresol); benzene-1,2-diol (catechol); and 1,6-anhydro-β-D-glucopyranose (levoglucosan). A stock solution was prepared using 0.5 ± 0.1 mg of each compound listed above, and this was dissolved in GC-grade ethanol in a 50 ml volumetric flask. The stock solution was then diluted into the following calibration solutions using additional GC-grade ethanol: 500, 800, 1200, 2000 and 4000 μg/ml. 1 μl of each of the calibration solutions was then separately analysed. These were introduced by evaporation, using the pyroprobe (CDS 5200 pyrolyser), at a heating rate of 100 °C/min and final temperature of 280 °C. A heated transfer line, maintained at 310 °C, was used to transfer the evaporated compounds onto the GC column. Calibration curves were derived and the curve linearity (r^2) was greater than 0.9434. GC–MS parameters are identical to those used for the analytical pyrolysis experiments.

2.6. Fast pyrolysis

Biomass was fed continuously by a volumetric screw feeder, using a single fast screw, into a 1 kg/h bubbling fluidized bed reactor (see Fig. 1) [30]. Nitrogen was used as the fluidizing gas; this was pre-heated prior to entry into the reactor and was not recycled. Approximately 1 kg of quartz sand was used as bed material, with a sand particle size range between 710 and 850 μm. The fast pyrolysis processing parameters are shown in Table 3. A quench column, cooled by a water cooling jacket, was used to condense condensable vapours, using ISOPAR at 30 °C as quenching medium. Aerosols were separated using a wet electrostatic precipitator (ESP) flushed with ISOPAR. The main condensate from the quench column and the wet ESP, commonly known as bio-oil, was collected in a common tank as shown in Fig. 1 (6 – common tank). The ISOPAR was recycled (skimmed from the top of the common tank) to the quench column and ESP. The remaining condensable light volatiles and vapours were condensed by a water cooled heat

Table 3
Fast pyrolysis processing parameters.

Parameter	Wheat straw	Switch grass	Miscanthus	Willow SRC [30]	Beech wood
Average feeding rate (g/h)	403.18	499.83	468.57	418.50	484.86
Feedstock particle size (mm)	0.25–1.00	0.25–1.00	0.25–1.00	0.25–1.00	0.25–1.00
Average pyrolysis temperature (°C)	525	510	505	500	512
Run time (min)	107	121	210	120	203
Biomass moisture content (%)	4.60	6.20	8.71	6.50	10.42
Biomass used (w.b) (g)	719	1008	1640	837	2551
Hot vapour residence time (s)	<1.5	<1.5	<1.5	<1.5	<1.5

(w.b) – wet basis.

exchanger (10 °C) and two dry ice cooled heat exchangers (−70 °C) set up in series. The collected condensates are referred to as secondary condensates. Non-condensable gases passed through a cotton wool filter before they were metered with a diaphragm gas meter, and analysed online using a Varian CP 4900 Micro-GC for nitrogen, hydrogen, CO, CO_2 and hydrocarbons up to C4. Experimental temperatures were measured with K-type thermocouples and were monitored and recorded using a Microlink 751 ADC unit in conjunction with the Windmill data logging software package. All products were carefully recovered and the mass balance was determined gravimetrically. The water content of the main liquid and secondary condensates was determined using the Karl Fisher volumetric titration. The water content of the feedstock and the products was used to calculate the reaction water found in the bio-oil.

The standard error was calculated for the mean of the three pyrolysis runs using willow SRC, and this is presented in Table 6. The standard error reflects the systematic error of measurement, and is provided here as an indication of the reliability and consistency of the measurements reported. Overall, it is evident that the values of the standard errors are relatively low, giving confidence in the measurement accuracy of the experiments that were conducted.

2.7. GC–MS analysis of bio-oil

The PerkinElmer Turbo Mass Gold GC–MS system and Varian GC-450 chromatograph and MS-220 mass spectrometer were used to analyse the chemical composition of the bio-oil. GC samples were prepared by mixing GC grade ethanol with bio-oil at a volume ratio of 5:1. For each system setup 1 μl of GC sample was injected onto the GC column, helium was used as the carrier gas and the mass spectra were obtained for a molecular mass range (m/z) of 45–300.

The PerkinElmer Turbo Mass Gold GC–MS system was used for the analyses of bio-oil generated from miscanthus and willow SRC. The injection port was kept at 280 °C and a 1:25 split ratio was used. The separation was carried out using a PerkinElmer Elite-1701 column (crossbond: 14% cyanopropylphenyl and 85% dimethyl polysiloxane; 60 m, 0.25 mm i.d., and 0.25 mm df). The GC oven was held at 45 °C for 5 min, then heated at 5 °C/min to 250 °C and held at this temperature for 5 min. Proposed peak assignments were made from mass spectra detection using the NIST98 MS library and from assignments in the literature [35,36].

The Varian 450-GC gas chromatograph and 220-MS mass spectrometer were used for the analyses of bio-oil generated from wheat straw, beech wood and switch grass. A Varian factorFour® column was used (30 m, 0.25 mm i.d., and 0.25 μm df). The injection port was kept at 275 °C and a 1:75 split ratio was used. The GC oven was held at 45 °C for 2.5 min, then heated at 5 °C/min to 250 °C and held at this temperature for 7.5 min. Proposed peak assignments ($m/z = 45$–300) were made from mass spectra detection using the NIST05 MS library and from assignments in the literature [35,36].

3. Results and discussion

3.1. Biomass characterisation

Comparisons of the ultimate, proximate and inorganic analyses, as well as the higher and lower heating values of the feedstocks investigated are shown in Table 4. From the ultimate analysis the hardwoods were seen to have a higher content of carbon and lower of oxygen. As a result, the calculated higher and lower heating values were found to be higher for the woody feedstocks. Results from the proximate analysis, show that higher amounts of volatile matter are obtained from beech wood (85.89 wt.%) and switch grass (83.23 wt.%). Ash content values were similar for the straw and

Table 4
Proximate, ultimate and inorganic analysis.

Analysis	Wheat straw [37]	Switch grass [37]	Miscanthus	Willow SRC [30]	Beech wood
Ultimate analysis (%$^{(\text{d.b})}$)					
C	44.93	46.21	46.95	48.48	53.04
H	5.71	5.80	5.85	5.74	5.42
N	0.63	0.40	0.92	1.87	-
O[a]	48.73	47.59	46.28	43.91	41.63
Proximate analysis (%)					
Moisture	4.56	4.61	4.55	5.71	4.24
Volatile matter $^{(\text{d.b})}$	79.92	83.23	75.62	81.19	85.89
Fixed carbon $^{(\text{d.b})}$	15.18	11.04	19.92	15.85	13.15
Ash $^{(\text{d.b})}$	4.89	5.73	4.46	2.96[b]	0.96
Heating value (MJ/kg)					
HHV $^{(\text{d.b})}$	17.25	17.90	18.38	19.06	20.55
LHV $^{(\text{d.b})}$	16.00	16.63	17.10	17.81	19.37
Inorganic analysis (%$^{(\text{d.b})}$)					
Al	0.01	0.02	–	0.03	–
Ca	0.51	0.50	0.18	1.15	0.27
Fe	0.02	0.01	–	0.02	–
K	0.57	0.09	1.20	0.59	0.14
Mg	0.07	0.06	0.15	0.16	0.04
Mn	0.01	–	–	0.01	0.01
Na	0.01	0.02	–	0.01	0.01
Ni	–	–	–	–	–
P	0.04	0.05	0.07	0.19	0.01
Pb	–	–	–	–	–
S	0.09	0.06	0.04	0.14	0.02
Zn	–	–	–	0.02	–

d.b – dry basis; – – not detected.
[a] By difference.
[b] Ash content analysis repeated for this study.

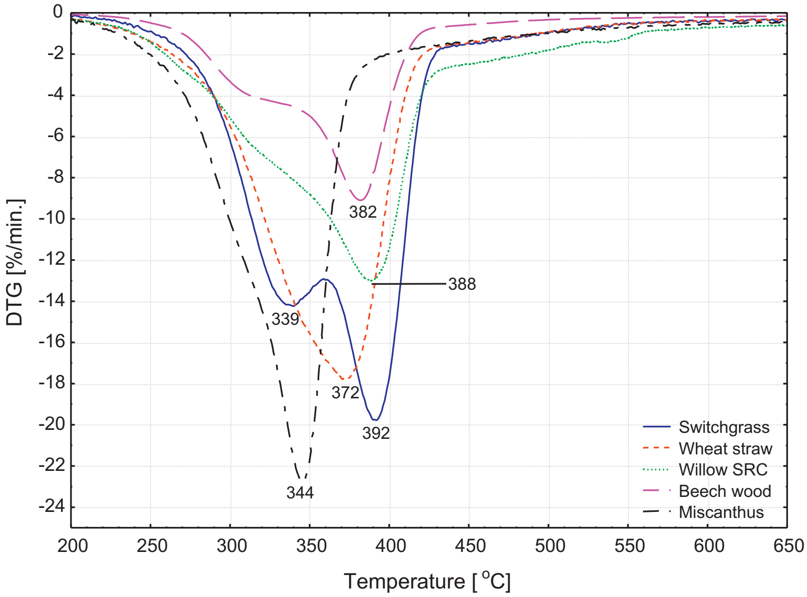

Fig. 2. Differential thermogravimetric pyrolysis profiles (switch grass and wheat straw results taken from [37] and willow [30]).

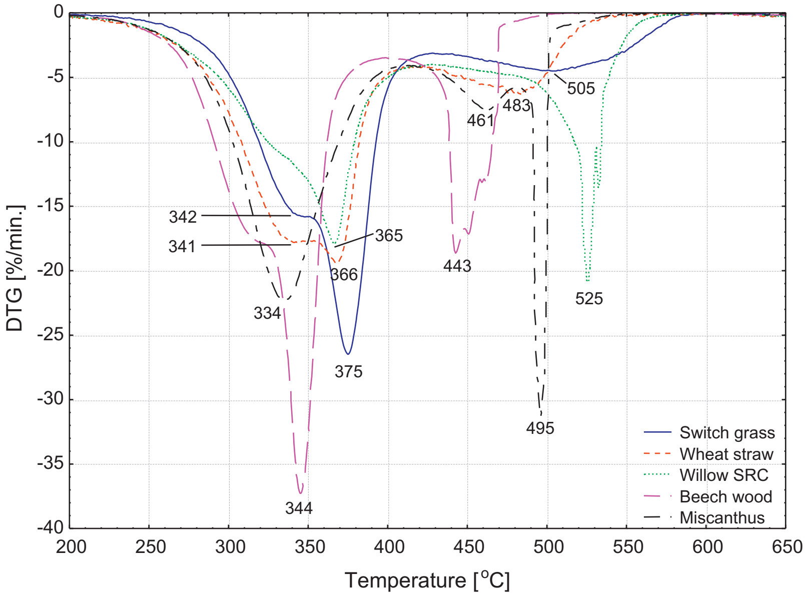

Fig. 3. Differential thermogravimetric combustion profiles (switch grass and wheat straw results taken from [37]).

perennial grasses, and lowest for the hardwood, beech wood (0.96 wt.%) and willow (2.96 wt.%). The inorganic content in willow SRC is anticipated to be higher than that of beech wood, because of the different plant growth periods. Switch grass also contained low levels of inorganics, but the ash content was higher. This may be attributed to the high levels of silica found in the perennial grasses [38]. Willow SRC contained the highest levels of calcium, magnesium, phosphorus and sulphur, and miscanthus had the highest level of potassium (1.20%). The addition of fertiliser and the time of harvest have a noticeable impact on the feedstock inorganic levels [39]. Wheat straw is grown commercially for its grain, and the fertiliser treatment is expected to be higher than that of perennial grasses and hardwoods. Switch grass did not receive any further fertiliser treatment after initial setup, and was harvested after the crop senesced. The time of harvest has been reported to influence inorganic content, particularly potassium, in the standing crop [39]. Nutrient remobilisation caused by weathering and leaching during the winter months is likely the primary cause. Miscanthus received additional fertiliser treatment and was harvested early, prior to the crop senescing. This is the probable cause for the high potassium content in miscanthus. Dust and soil adhesion to the crop sample could possibly further increase the inorganic content.

3.2. Thermal decomposition studies (TGAs)

The differential thermogravimetric pyrolysis and combustion profiles can be found in Figs. 2 and 3 respectively. The differential

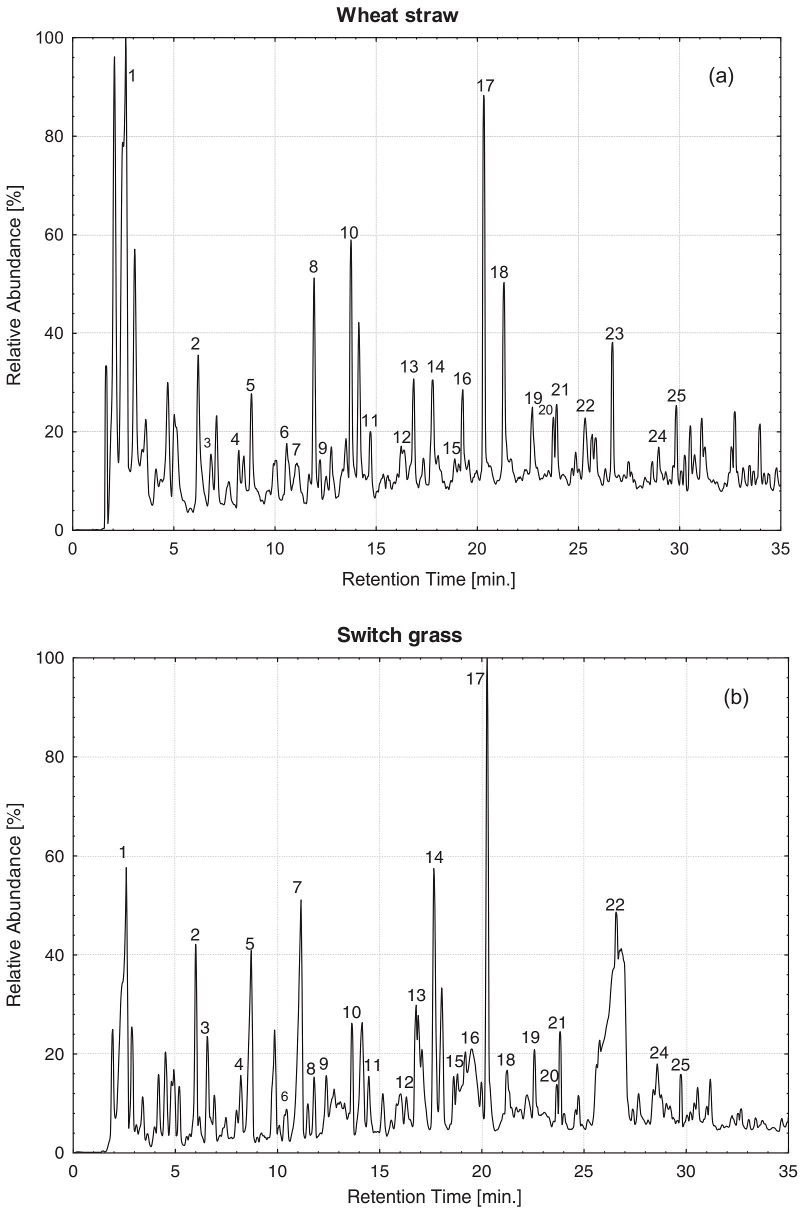

Fig. 4. (a) *Py-GC–MS chromatogram for **wheat straw***: (1) acetic acid; (2) furfural; (3) 2-furanmethanol; (4) 2(5H)-furanone; (5) 1,2-cyclopentanedione; (6) phenol; (7) butanedioic acid; (8) 3-methyl-1,2-cyclopentanedione; (9) 2-methylphenol; (10) guaiacol; (11) 3-ethyl-2-hydroxy-2-cyclopentene-1-one; (12) 2-methoxy-4-methylphenol; (13) catechol; (14) 3-methyl-benzaldehyde; (15) 3-methoxycatechol; (16) 4-ethyl-2-methyl-phenol; (17) 2-methoxy-4-vinylphenol; (18) 2,6-dimethoxy-phenol; (19) vanillin; (20) 1,2,4-trimethoxybenzene; (21) 2-methoxy-6-(2-propenyl)-phenol; (22) levoglucosan; (23) 3′5′-dimethoxyacetophenone; (24) syringaldehyde; and (25) 2,6-dimethoxy-4-(2-propenyl)-phenol. (b) *Py-GC–MS chromatogram for **switch grass*** [37]: (1) acetic acid; (2) furfural; (3) 2-furanmethanol; (4) 2(5h)-furanone; (5) 1,2-cyclopentanedione; (6) phenol; (7) butanedioic acid; (8) 3-methyl-1,2-cyclopentanedione; (9) 2-methylphenol; (10) guaiacol; 11) 3-ethyl-2-hydroxy-2-cyclopentene-1-one; (12) 2-methoxy-4-methylphenol; (13) catechol; (14) 3-methyl-benzaldehyde; (15) 3-methoxycatechol; (16) 4-ethyl-2-methyl-phenol; (17) 2-methoxy-4-vinylphenol; (18) 2,6-dimethoxy-phenol; (19) vanillin; (20) 1,2,4-trimethoxybenzene; (21) 2-methoxy-6-(2-propenyl)-phenol; (22) levoglucosan; (23) 3′5′-dimethoxyacetophenone; (24) syringaldehyde; and (25) 2,6-dimethoxy-4-(2-propenyl)-phenol. (c) *Py-GC–MS chromatogram for **miscanthus***: (1) acetic acid; (2) furfural; (3) 2-furanmethanol; (4) 2-methyl-2-cyclopenten-1-one; (5) cyclopentanedione; (6) phenol; (7) 3,4-dihydroxy-3-cyclobutene-1,2-dione; (8) 2-hydroxy-3-methyl-2-cyclopenten-1-one; (9) guaiacol; (10) tetrahydro-2-furnanmethanol; (11) 2-methoxy-4-methylphenol;12) catechol; (13) 3-methyl-benzaldehyde;14) 3-methoxycatechol; (15) 3-methoxy-4-vinylphenol; (16) 2,6-dimethoxy-phenol; (17) vanillin; (18) 1,2,4-trimethoxybenzene; (19) 2-methoxy-6-(2-propenyl)-phenol; (20) levoglucosan; (21) 3′5′-dimethoxyacetophenone; (22) syringaldehyde; and (23) 2,6-dimethoxy-4-(2-propenyl)-phenol. (d) *Py-GC–MS chromatogram for **willow SRC***: (1) acetic acid; (2) furfural; (3) 2-furanmethanol; (4) 1,2-cyclopentanedione; (5) phenol; (6) 3,4-dihydroxy-3′-cyclobutene-1,2-diol; (7) guaiacol; (8) 2-methoxy-4-methylphenol; (9) catechol; (10) 3-methoxycatechol; (11) 2-methoxy-4-vinylphenol; (12) 2,6-dimethoxy-phenol; (13) vanillin; (14) 1,4:3,6-dianhydro-α-D-glucopyranose; (15) levoglucosan; (16) 3′5′-dimethoxyacetophenone; (17) syringaldehyde; and (18) 2,6-dimethoxy-4-(2-propenyl)-phenol. (e) *Py-GC–MS chromatogram for **beech wood***: (1) acetic acid; (2) furfural; (3) 2-furanmethanol; (4) 1,2-cyclopentanedione; (5) phenol; (6) 3,4-dihydroxy-3′-cyclobutene-1,2-diol; (7) guaiacol; (8) 2-methoxy-4-methylphenol; (9) catechol; (10) 3-methoxycatechol; (11) 2-methoxy-4-vinylphenol; (12) 2,6-dimethoxy-phenol; (13) vanillin; (14) 1,4:3,6-dianhydro-α-D-glucopyranose; (15) levoglucosan; (16) 3′5′-dimethoxyacetophenone; (17) syringaldehyde; (18) 2,6-dimethoxy-4-(2-propenyl)-phenol.

thermogravimetric profile (DTG), the first derivative of the TGA profile, reports the percentage weight loss per minute as a function of temperature. The shape of the DTG profile is correlated to the compositional content of the crop [40,41]. This is largely reflective of the cellulose, hemicellulose, lignin and inorganic content. From the DTG pyrolysis profile, shown in Fig. 2, it can be seen that the maximum rate of thermal degradation occurs between 339°C and 392 °C for all feedstocks. The hardwoods are found to have lower maximum thermal decomposition rates and these are seen to occur at higher temperatures. This is partly related to the higher lig-

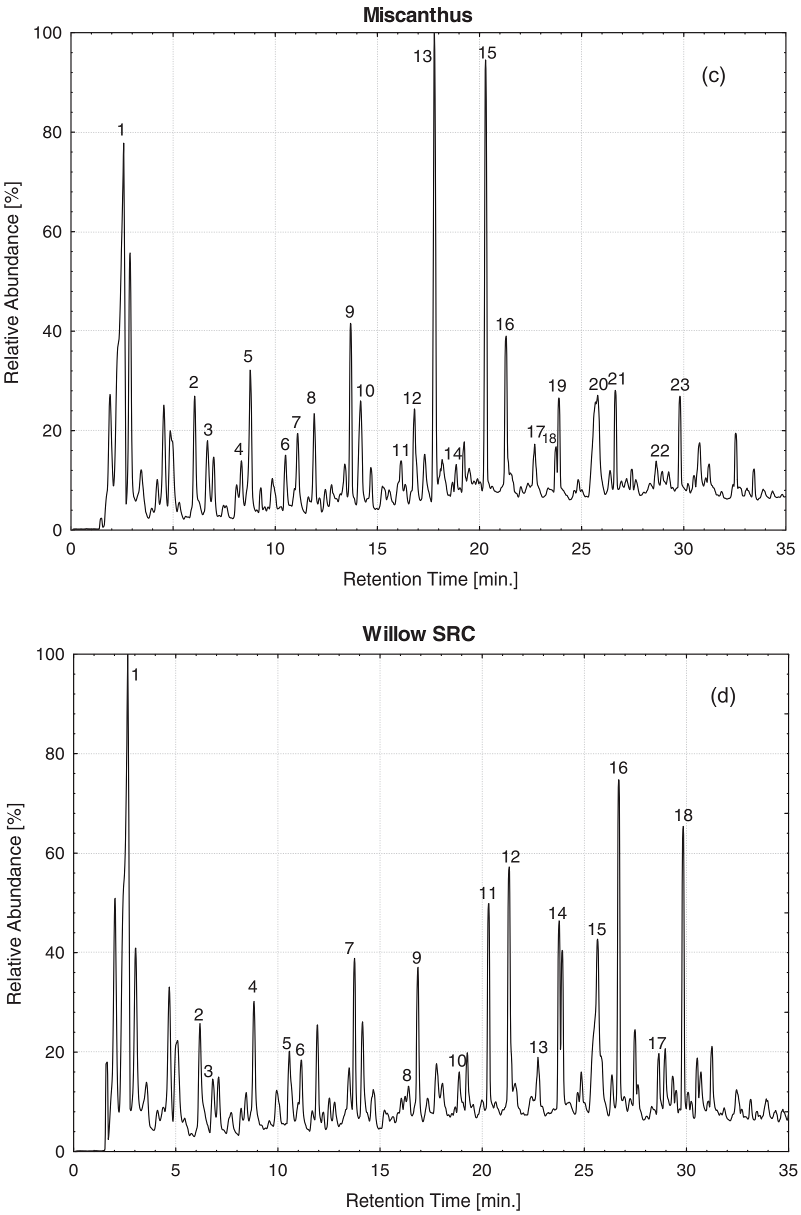

Fig. 4. (*continued*)

nin content, which constitutes a major part of the overall structure of hardwoods. Miscanthus has a maximum decomposition rate at the lowest temperature when compared to the other feedstocks.

The catalytic impact of potassium is thought to be major contributor to the occurrence of the maximum decomposition rate. The shoulder-like features on the DTG curves can be seen for both beech wood and switch grass, and are probably representative of the hemicellulose content. Based on data shown in Table 1, the ratio of hemicellulose to cellulose in switch grass was found to be the highest, and its shoulder-like feature is most prominent. Varhegyi et al. showed that the thermal decomposition of hemicellulose takes place at a lower temperature when compared to cellulose [42]. Yang et al. reported that the thermal decomposition of lignin occurs over a broad temperature range, and partially contributes to the cellulose and hemicellulose regions [43].

The DTG combustion profile shown in Fig. 3 shows two distinct decomposition regions. The first decomposition region occurs below 400 °C, and this is representative of the initial volatile combustion. The temperature of the maximum rate of decomposition is seen to be highest for switch grass, and lowest for miscanthus. The catalytic impact of potassium is assumed to be responsible for the differences seen between the perennial grasses. The second decomposition region, after 400 °C, is reflective of the char burnout. The hardwoods were found to have distinct broad regions and this appears to be related to the lignin content. Ghetti et al. showed that the first region of decomposition is associated with the combustion of hemicellulose and cellulose, and the second with the combustion of lignin [44]. This is because lignin is more aromatic than cellulose and hemicellulose, and therefore requires more energy to break the bonds.

3.3. Analytical pyrolysis (Py-GC–MS)

Fig. 4 show the pyrolysis-gas chromatography–mass spectrometry chromatograms for all feedstocks investigated. From Fig. 5, notable differences were seen in the content of 1,2-cyclopentanedione (cellulose marker), butanedioic acid, dimethyl ester (hemicelluloses decomposition products) and catechol (lignin

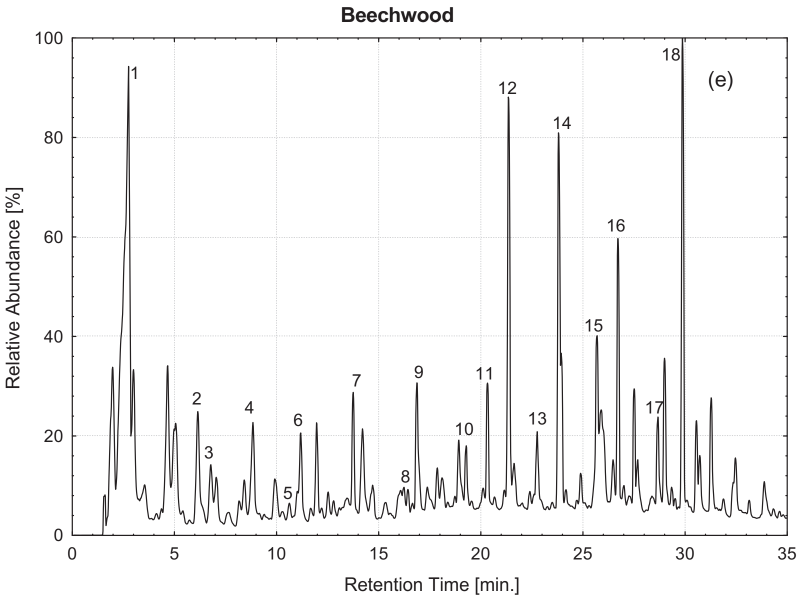

Fig. 4. (*continued*)

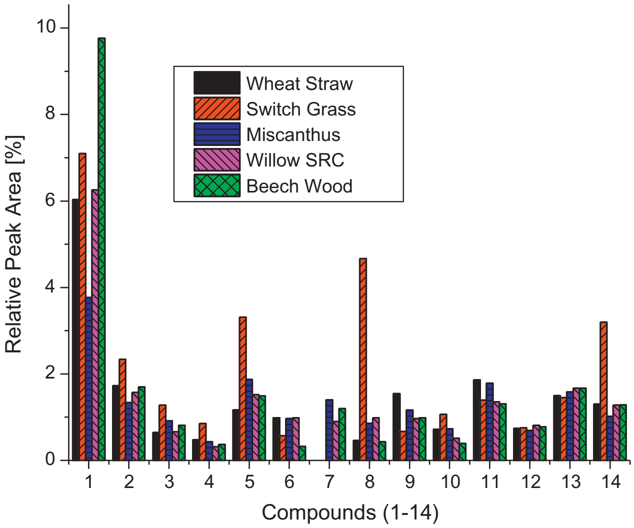

Fig. 5. Relative peak area comparison of key pyrolysis products from wheat straw, switch grass, miscanthus, willow SRC and beech wood. (1) Acetic acid; (2) furfural; (3) 2-furanmethanol; (4) 2(5H)-furanone; (5) 1,2-cyclopentanedione; (6) phenol; (7) 3,4-dihydroxy-3-cyclobutene-1,2-dione; (8) butanedioic acid; (9) 3-methyl-1,2-cyclopentanedione; (10) 2-methylphenol; (11) guaiacol; (12) 3-ethyl-2-hydroxy-2-cyclopentene-1-one; (13) 2-methoxy-4-methylphenol; and (14) catechol.

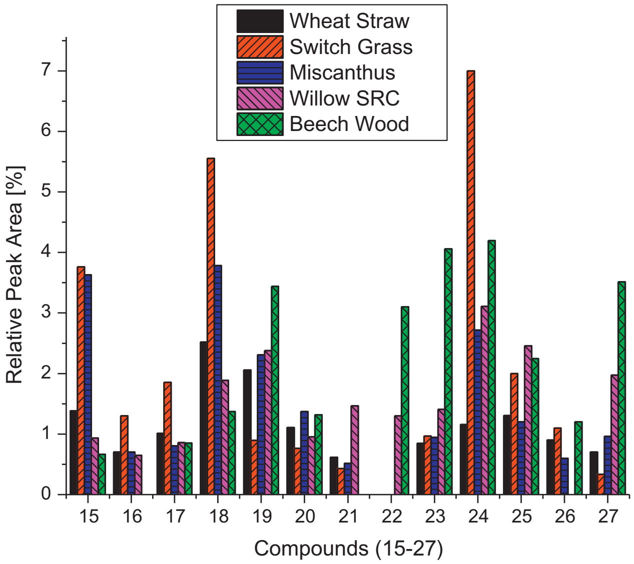

Fig. 6. Relative peak area comparison of key pyrolysis products from wheat straw, switch grass, miscanthus, willow SRC and beech wood. (15) 3-Methyl-benzaldehyde; (16) 3-methoxycatechol; (17) 4-ethyl-2-methyl-phenol; (18) 2-methoxy-4-vinylphenol; (19) 2,6-dimethoxy-phenol; (20) vanillin; (21) 1,2,4-trimethoxybenzene; (22) 1,4:3,6-dianhydro-α-D-glucopyranose; (23) 2-methoxy-6-(2-propenyl)-phenol; (24) levoglucosan; (25) 3′5′-dimethoxyacetophenone; (26) syringaldehyde; and (27) 2,6-dimethoxy-4-(2-propenyl)-phenol.

decomposition product) for switch grass. The other feedstocks, produced similar yields for the remaining compounds identified and no further major difference was seen, except for beech wood which had the highest content of acetic acid. From Fig. 6, larger differences were seen between the different feedstock. Switch grass was found to produce the highest yields of 2-methoxy-4-vinylphenol (guaiacyl lignin decomposition product) and levoglucosan, an intermediate pyrolytic decomposition product of cellulose. Beech wood was seen to produce a high content of 2,6-dimethoxy-phenol (syringyl lignin decomposition product), 1,4:3,6-dianhydro-α-D-glucopyranose (a cellulose decomposition product), 2-methoxy-6-(2-propenyl)-phenol (guaiacyl lignin decomposition product) and 2,6-dimethoxy-4-(2-propenyl)-phenol (syringyl lignin decomposition product). Willow SRC was seen to have highest level of 1,2,4-trimethoxybenzene (guaiacyl lignin decomposition product), and miscanthus was found to have similar levels to switch grass for the lignin decomposition product 3-methyl-benzaldehyde. Key products, such as 3-methyl-1,2-cyclopentanedione (cellulose) and 2-methoxyphenol (guaiacyl lignin marker) in Fig. 5 were found to be highest in wheat straw.

Key pyrolysis decomposition products have been quantified and these are shown in Table 5. A graphical representation of the data presented in Table 5 is presented in Fig. 7. For the perennial grasses, switch grass was found to have the highest yield of furfural (0.571 wt.%), 2-furanmethanol (0.183 wt.%), levoglucosan (0.728 wt.%), 1,2-benzenediol (0.265 wt.%) and 2-methoxy-4-

Table 5
Py-GC–MS of feedstock – compound quantification and calibration accuracy.

Compound name	Type of key marker	Calibration r^{2a}	Yield (wt.% (d.a.f))				
			Wheat straw	Switch grass	Miscanthus	Willow SRC	Beech wood
Furfural	C, X	0.9434	0.391	0.571	0.141	0.16	0.533
2-Furanmethanol	C	0.9801	0.05	0.183	0.079	0.074	0.011
Phenol	C, L	0.9983	0.031	0.024	0.036	0.063	0.004
Guaiacol	L	0.9981	0.071	0.068	0.06	0.053	0.096
2-Methoxy-4-methylphenol	GL	0.9979	0.025	0.039	0.019	0.026	–
1,2-Benzenediol	L	0.9946	0.144	0.265	0.052	0.057	0.009
2-Methoxycatechol	L	0.9949	0.025	0.011	0.022	0.022	0.006
2-Methoxy-4-vinylphenol	GL	0.9818	0.255	0.375	0.148	0.09	0.237
Vanillin	GL	0.9926	0.042	0.051	0.018	0.018	0.039
Levoglucosan	C	0.9834	0.01	0.728	0.02	0.086	0.006
Syringaldehyde	L	0.9925	0.025	0.015	0.019	0.026	0.088
Total			1.07	2.33	0.61	0.68	1.03

C – cellulose; L – lignin; GL – guaiacyl lignin; X – xylan; – – not detected.
[a] Quantified using 5 different concentrations.

Table 6
Fast pyrolysis mass balance on dry basis (wt.%).

Products	Feedstock				**Standard error estimation using Willow SRC**			
	Wheat straw	Switch grass	Miscanthus	Beech wood	Run 1 [30]	Run 2	Run 3	Standard error
Char total	**28.05**	**20.03**	**31.37**	**14.43**	**19.28**	**19.98**	**20.18**	**0.22**
Bio-oil total	**34.97**	**57.90**	**46.61**	**63.17**	**51.34**	**58.68**	**60.81**	**2.34**
Organics	21.39	45.36	40.53	55.47	40.51	48.64	43.98	1.92
Reaction water	13.58	12.54	6.08	7.70	10.83	10.04	16.83	1.75
Gas total	**26.99**	**16.57**	**9.13**	**13.03**	**19.89**	**17.94**	**17.02**	**0.69**
H_2	0.85	0.59	0.76	0.64	0.78	0.05	0.03	0.20
CO	8.44	5.90	4.36	6.09	9.22	5.70	5.39	1.00
CH_4	1.95	1.20	0.78	0.14	1.45	0.67	10.50	2.58
CO_2	11.11	5.88	2.76	5.81	7.71	11.00	0.60	2.51
Ethene	0.73	0.62	0.23	0.14	0.32	0.13	0.13	0.05
Ethane	0.80	0.58	0.15	0.10	0.16	0.16	0.11	0.01
Propene	1.48	0.53	0.07	0.08	0.19	0.06	0.16	0.03
Propane	0.92	0.68	0.01	0.02	0.04	0.15	0.08	0.03
n-Butane	0.71	0.59	0.01	0.01	0.02	0.02	0.02	0.00
Closure	**90.01**	**94.50**	**87.11**	**90.63**	**90.51**	**96.60**	**98.01**	**1.88**

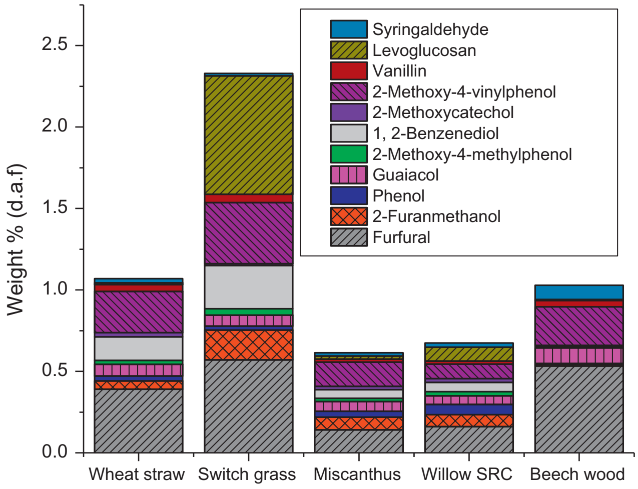

Fig. 7. Comparison of compound peak areas between the different feedstocks.

vinylphenol (0.375 wt.%). The yield of 3-methoxycatechol was highest for wheat straw. In contrast to the perennial grasses and straws, the hardwood willow SRC produced higher yields of phenol (0.325 wt.%), and beech wood generated higher yields of guaiacol (0.096 wt.%) and syringaldehyde (0.088 wt.%). The short hold time at the pyrolysis temperature is thought to be the cause for the low yields found. Longer hold times have been shown to influence the yields of the compounds produced [30].

3.4. Laboratory scale fast pyrolysis experiments

The fast pyrolysis process conditions and mass balances are shown in Table 3 and 6 respectively. Losses in the mass balance are thought to be caused by errors in weight measurement, water content analysis, liquid holdup within the quench system and gas analysis errors caused by heavily diluted pyrolysis gases, with content of nitrogen above 97%.

A graphical representation of the data in Table 6 can be found in Fig. 8. This clearly shows the differences in pyrolysis yields between feedstocks. The organic liquid yield was highest for beech wood and lowest for wheat straw. From the preliminary thermogravimetric data presented in Table 4, beech wood had the highest weight percentage of volatile matter and lowest of char. Switch grass was found to produce high organic liquid yields irrespective of the ash content. This is thought to be related to the lower level of potassium within switch grass. The other perennial grass miscanthus, produced similar organic liquid yields to willow SRC. When compared to willow SRC, wheat straw had lower calcium levels and similar potassium levels. The reduced organic liquid yield in

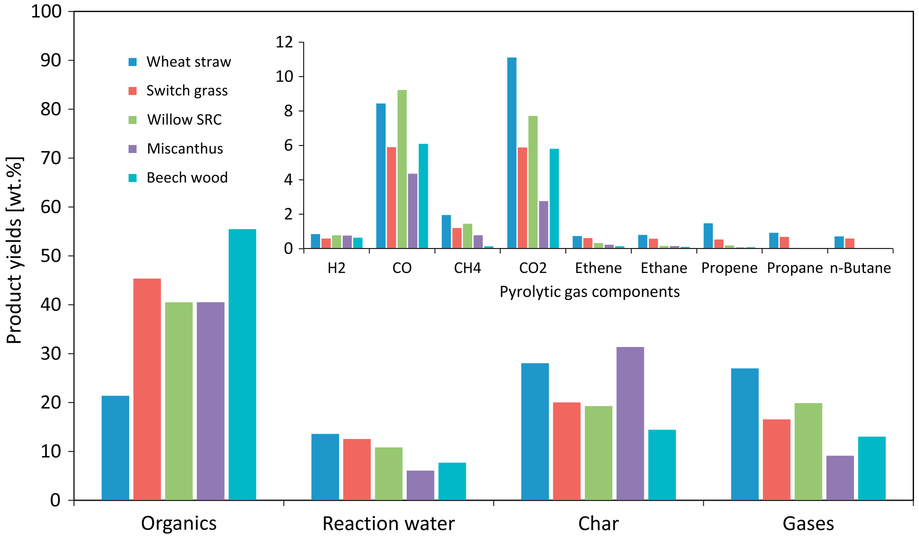

Fig. 8. Mass balance and gas analysis on dry basis for wheat straw, switchgrass, willow SRC [30], miscanthus and beech wood.

Table 7
Bio-oil and char analysis.

	Wheat straw[b]	Switch grass	Miscanthus	Willow SRC	Beech wood
Bio-oil					
Water content (wt.%)	22.10	21.60	22.00	15.00	12.80
pH	4.10	3.39	3.78	3.42	2.86
Homogeneity	Phase-separated	Single phase	Single phase	Single phase	Single phase
Elemental composition (wt.% d.b)					
Carbon	60.33	63.15	54.90	62.94	54.24
Hydrogen	8.61	7.97	7.40	5.86	6.90
Nitrogen	1.05	0.73	1.63	0.11	0.00
Oxygen[a]	30.01	28.15	36.07	31.09	38.86
Heating values (MJ/kg)					
HHV (a.r)	22.0	22.3	18.8	21.8	20.1
LHV (a.r)	20.0	20.4	17.0	20.3	18.4
Char					
Elemental composition (wt.% d.b)					
Carbon	60.45	56.47	62.31	61.97	73.45
Hydrogen	2.67	2.76	3.00	3.37	3.21
Nitrogen	0.63	0.69	1.12	0.88	0.17
Oxygen[a]	25.99	27.45	23.04	24.51	20.6
Ash (wt.% d.b)	10.26	12.63	10.53	9.27	2.57
Heating values (MJ/kg)					
HHV (d.b)	22.3	20.9	22.9	22.8	26.8
LHV (d.b)	21.7	20.3	22.3	22.1	26.1

a.r – as received (wet basis); d.b. – dry basis.
[a] By difference.
[b] Analysis of bottom phase of bio-oil.

wheat straw is caused by the higher production of non-condensable gases and reaction water. The gas analysis shows that the yields of non-condensable gases such as carbon dioxide, methane, ethane, propene, propane and *n*-butane are highest for wheat straw. A possible cause for the high non-condensable gases is thought to be related to the potassium content.

A number of similarities and differences can be seen when comparing obtained results with reported results (presented in Table 2). A large number of authors did not report on the reaction water generated. Similar values of char content were found for the feedstock investigated, except for miscanthus. The low char yield reported by Hodgson et al. is thought to be linked to the reduced reactor capacity and amount of feedstock used. Char content results presented by Fahmi et al. for wheat straw, switch grass and willow SRC, using a smaller capacity reactor, were found to be very similar. The char yield of beech wood was found to be the lowest and results are similar to those presented by Wang et al. The ash content of the feedstock significantly contributes to the overall char yield. The overall bio-oil yield was reported in to be highest for beech wood and this corresponds well with our finding. The organic content, reported by Fahmi et al. for switch grass and willow SRC were similar to that reported here; wheat straw was found to have a value approximately 10% lower.

3.5. Product characterisation

The properties of the bio-oils produced are shown in Table 7. The straw and perennial grasses were found to have the highest

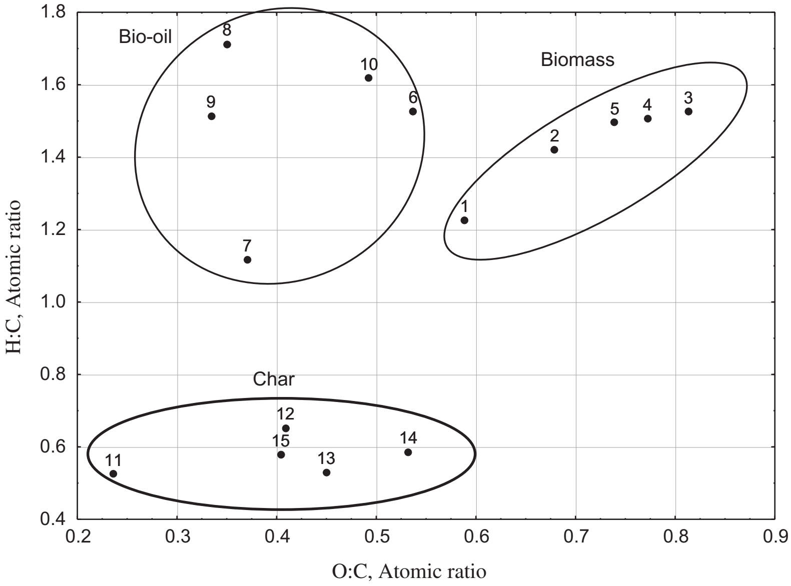

Fig. 9. Van Krevelen diagram – H:C and O:C atomic ratios of biomass, fast pyrolysis char and fast pyrolysis bio-oil on dry basis. (Biomass feedstock – beech wood 1; willow SRC 2; wheat straw 3; switch grass 4; miscanthus 5); (Bio-oil – beech wood 6; willow SRC 7; wheat straw 8; switch grass 9; miscanthus 10); (char– beech wood 11; willow SRC 12; wheat straw 13; switch grass 14; miscanthus 15).

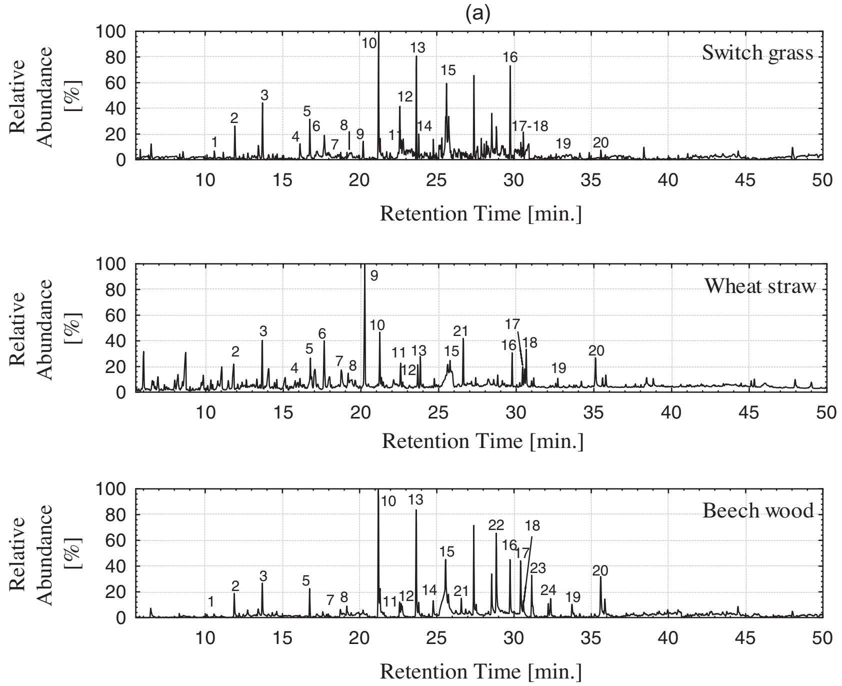

Fig. 10. (a) Bio-oil chromatograms for switch grass, wheat straw and beechwood. Peak assignments: (1) phenol; (2) 3-methyl-1,2-cyclopentanedione; (3) 2-methoxyphenol; (4) 1,4-benzenedimethanol; (5) 2-methoxy-4-methyl-phenol; (6) 2-methyl, benzaldehyde; (7) 3-methoxy-1,2-benzenediol; (8) 4-ethyl-2-methoxy-phenol; (9) 2-methoxy-4-vinylphenol; (10) 2,6-dimethoxy-phenol; (11) isovanillin; (12) vanillin; (13) 1,2,4-trimethoxybenzene; (14) 2-methoxy-4-propenyl-phenol; (15) 2,5-dimethoxybenzoic acid; (16) 2,6-dimethoxy-4-(2-propenyl)-phenol; (17) 2,4,5-trimethoxy-benzaldehyde; (18) 4-hydroxy-2-methoxycinnamaldehyd; (19) 2,3,4-trimethoxybenzoic acid; (20) asarone; (21) 3′,5′-dimethoxyacetophenone; (22) 4-hydroxy-3,5-dimethoxy-benzaldehyde; (23) desaspidinol; (24) 1,2,5-dimethoxybenzylacetate. (b) Bio-oil chromatograms for willow SRC and miscanthus. Peak assignments: (1) 3-hydroxy-2-butanone; (2) furfural; (3) 1,4-dimethyl-pyrazole; (4) 1,3-cyclohexanediol; (5) 2-methyl-furan; (6) hexanoic acid; (7) 1-(acetyloxy)-2-propanone; (8) 2-methyl-2-cyclopenten-1-one; (9) 2-methyl-propanoic acid; (10) 2-ethyl-3-methyl-2-pentanol; (11) 2-butenoic acid; (12) 4-hydroxy-butanoic acid; (13) 2- and/or 3-methyl-2-cyclopenten-1-one; (14) cyclopentanone; (15) 3,4-dimethyl-2-pentene; (16) 4-methyl-2-pentene; (17) 3-penten-2-ol; (18) 2-methoxy-phenol or/and 19) 2-methyl-phenol; (20) 2-(2-propenyl)-furan; (21) maltol; (22) 4-ethyl-2-methoxy-phenol; (23) 2,3- and/or 3,4-anhydrogalactosan; (24) 1-(2-hydroxy-methylphenyl)-ethanone; (25) eugenol; (26) phenol; (27) 2-methoxy-4-(1-propenyl)-phenol; (28) 1,2,4-trimethoxybenzene; (29) vanillin; (30) 1,2,3-trimethoxy-5-methyl-benzene; (31) 1-(4-hydroxy-3-methoxyphenyl)-ethanone; (32) 2-methoxy-4-propenyl-phenol; (33) 2,6-dimethoxy-4-(2-propenyl)-phenol; (34) 2,5-dimethoxy-ethylbenzene; (35) 4-hydroxy-3,5-dimethoxy-benzaldehyde; (36) 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone; (37) 1-(2,4,6-trihydroxyphenyl)-2-pentanone; (38) 2,6-dimethoxyphenol; (39) 2,5-diethoxytetahydrofuran; (40) 4-hydroxy-butanoic acid; (41) 2,3-dimethylphenol; (42) 3,5-dimethylphenol; (43) 2- or/and 3- or/and 4-methylbenzaldehyde; (44) 1,2-benzenediol; (45) 2-methyl-1,3-benzenediol.

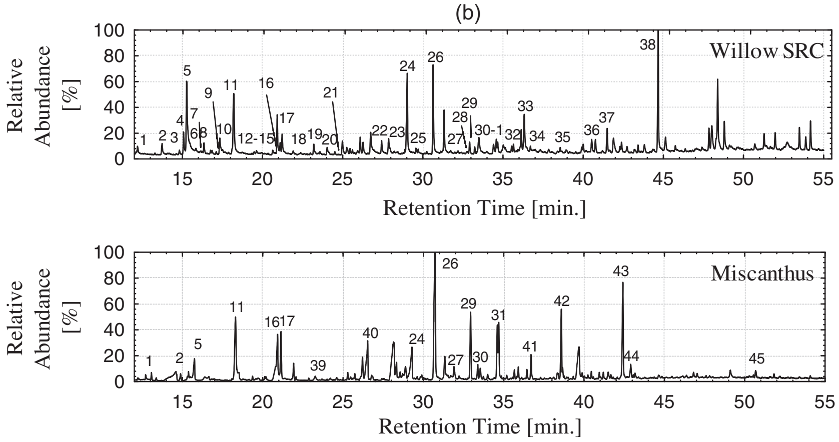

Fig. 10. (*continued*)

Table 8
Fraction of compounds in fast pyrolysis bio-oils.

Group of compounds	Wheat straw	Switch grass	Miscanthus	Willow SRC	Beech wood
	Yield (%)[a]				
Acids	4.59	3.25	2.75	3.21	8.78
Esters	3.78	4.23	5.68	3.28	4.23
Ethers	6.21	9.22	7.21	3.27	4.61
Aldehydes	8.45	10.26	9.87	8.32	7.22
Ketones	12.54	9.86	16.59	17.42	12.36
Alcohols	7.23	5.66	4.72	5.32	3.78
Furans	6.94	7.81	6.38	3.26	9.74
Phenols	21.34	18.95	19.65	28.59	23.85
Closure	71.08	69.24	72.85	72.67	74.57

[a] Yields are related to the peak area percentage (GC–MS chromatograms) in the bio-oil. Compounds with peak areas of less than 0.425% were not included.

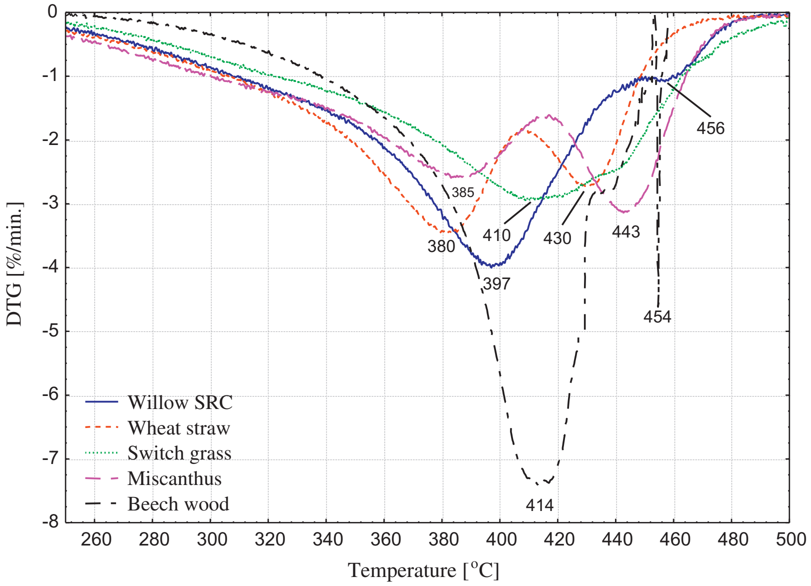

Fig. 11. Differential thermogravimetric combustion profiles of fast pyrolysis chars.

bio-oil water content. The water content is a combination of the initial feedstock moisture and the reaction water generated by thermal degradation reactions. The water content is relative to the initial feedstock moisture. He et al. reported that the bio-oil water content generally increases by increasing the initial feedstock moisture content [45]. The basic elemental analysis for the bio-oils and chars produced are shown in Table 7. The H:C and O:C atomic ratios for the feedstocks, bio-oils and chars are shown in Fig. 9. Three main clusters can be seen on the Van Krevelen diagram, and these are representative of the feedstocks, bio-oils and chars. Thermal conversion by fast pyrolysis has reduced the pyrolysis product O:C atomic ratio from 0.65–0.85 to 0.15–0.55, thus producing a more carbonaceous bio-oil and char product. The char H:C atomic ratio (0.40–0.70) was found to be very low when compared to the feedstocks and the bio-oils produced (1.70–1.10). The lower H:C and O:C atomic ratios in the chars are indicative of increased carbon–carbon bonds [3]. This is clearly evident when comparing the higher and lower heating values. The bio-oil higher heating values, as received basis, range from 18.8 to 22.3 MJ/kg and in most cases, except for miscanthus and beech wood, they are found to be higher than the chars; this is because of the high ash content in the chars. Switch grass bio-oil has the highest higher heating value of 22.3 MJ/kg, on as received basis.

The bio-oil obtained from wheat straw was phase separated, and the bottom layer was used for all analytical investigations. The bottom layer of the wheat straw bio-oil was seen to have a high viscosity. Oasmaa et al. investigated bio-oil phase separation and reported that feedstocks rich in extractives, e.g. forestry and agricultural residues, generally produce phase separation bio-oils [46]. The bottom layer is reported to exist in the form of a micro-emulsion, and this is stabilised by acids within that layer. The micro-emulsion can be destabilised by the addition of water. This is because water addition reduces the interaction between the acid and the micro-emulsion, ultimately resulting in a change in solubility and subsequent precipitation. The pH of wheat straw was found to be the least acidic (pH = 4.10). The higher pH value may be partly responsible for the phase separation seen in wheat straw. The main bio-oil generated was compared by GC–MS and the results are presented in Fig. 10. It can be observed that the bio-oils are mainly composed of oxygenated organic compounds such as organic acids, esters, ethers, aldehydes, ketones, alcohols, furans and phenols. Yields of these particular groups of compounds are given for comparison in Table 8.

The fast pyrolysis chars were analysed by thermogravimetric analysis and this is shown in Fig. 11. The maximum thermal degradation occurred between 380 °C and 443 °C. The ash content within the char is shown in Table 7. The char ash content is typically higher than the initial feedstock because the non-volatile inorganics will mainly remain within the char particle. Beech wood char was seen to have the highest higher heating value of 26.8 MJ/kg, and this is due to the low ash content found in the char.

4. Conclusions

Analytical and laboratory scale pyrolysis have been used to compare yields and products from straw, perennial grasses and hardwoods. From the analytical work, it was found that hardwoods have a high calorific value, and this is due to their higher carbon and lower ash content. Volatile matter was seen to be highest in beech wood and switch grass and lowest in miscanthus. Py-GC–MS quantification results show that the highest yields of furfural (0.571 wt.%), 2-furanmethanol (0.183 wt.%), levoglucosan (0.728 wt.%), 1,2-benzenediol (0.265 wt.%) and 2-methoxy-4-vinylphenol (0.375 wt.%) were found in switch grass, and that willow SRC produced the highest yield of phenol (0.325 wt.%).

From the laboratory processing, the organic yield was highest for beech wood and lowest for wheat straw. The bio-oil higher heating value was highest for switch grass (22.3 MJ/kg). Water content within the bio-oil is highest in the straw and perennial grasses, and lowest in the hardwood, willow SRC. The bio-oil produced from wheat straw was phase separated and had the highest pH value. Beech wood was found to have the lowest char ash content of 2.57 wt.%; as a result the calorific value was found to be highest when compared with other feedstocks.

In summary, the perennial grasses and hardwoods generate high bio-oil liquid yields that are homogeneous. The estimated production cost to produce switch grass, miscanthus and willow SRC are similar, but harvest yields are higher per hectare for miscanthus. The high bio-oil and char heating value and low water content found in willow SRC, makes this crop an attractive energy feedstock for fast pyrolysis processing, if the associated production costs and harvest yields can be maintained at current reported values. The bio-oil from switch grass has the highest potential for upgrading to produce high value chemicals.

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